Landau theory of the charge-density-wave state in tantalum diselenide under pressure

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It has recently been observed by McWhan and co-workers that the commensurate charge density wave in $2H$-$TaSe_2$ can be suppressed by a pressure $P \approx 2$ GPa only to reappear again at higher pressures. This behavior can be explained if the energy to introduce a discommensuration in the commensurate phase goes through a minimum. This can happen if the interlayer coupling causes the intralayer phase to move from one minimum to another. A quantitative discrepancy remains and it is suggested that this may be due to impurity pinning effects on the discommensurations.

I. INTRODUCTION

Charge density waves (CDW) have been observed and studied in many transition-metal dichalcogenides.[1,2] The most studied compound in this group is $2H$-$TaSe_2$. In the original neutron scattering experiments of Moncton, Axe, and Di Salvo[3] the onset of the CDW phase in an incommensurate phase (I) was observed at $T = 122$ K followed by a first-order transition to a commensurate CDW phase (C) at $T \approx 90$ K. The commensurate phase had a wave vector which was one third of a basal plane reciprocal-lattice vector. Recently a more detailed study[4] of this transition has revealed more complex behavior at the incommensurate-commensurate (IC) transition. Further high-pressure studies by McWhan, Fleming, Moncton, and DiSalvo[5] obtained an unusual reentrant behavior of C phase with pressure. Their phase diagram is shown in Fig. 1. The IC phase boundary initially drops rapidly with pressure and in the interval between 1.7 and 2.3 GPa the I phase is observed down to the lowest temperature. However, beyond 2.3 GPa the IC phase boundary rises rapidly and saturates. The C phase is observed to have the same wave vector as at low pressures, viz., one third of a basal plane reciprocal-lattice vector. The explanation of this reentrant phase diagram is the subject of this paper.

In the original study of the IC transition,[3] a simplified Landau model was used. This model of a single $\vec{Q}$ vector CDW was further studied by McMillan[6] who found a continuous IC transition whose onset is determined by the energy to introduce a discommensuration (DC) into the C phase. This theory in which only the phase of the CDW order parameter is allowed to vary, is equivalent to the theory of the registry transition of a film on a substrate introduced earlier by Frank and van der Merwe.[7] They obtained an analytic solution for the shape and energy of a DC. The effect of including variations in the amplitude of the order parameter in this theory has been studied by several groups.[8–10] Recently Jacobs and Walker[10] have shown that this leads to a first-order transition at higher temperatures. However in this work we are interested only in the general form of the phase diagram and we shall ignore amplitude variations.

The CDW phase of $2H$-$TaSe_2$ has three $\vec{Q}$ vectors which leads to a more complicated form of the free energy in a Landau expansion. The most general

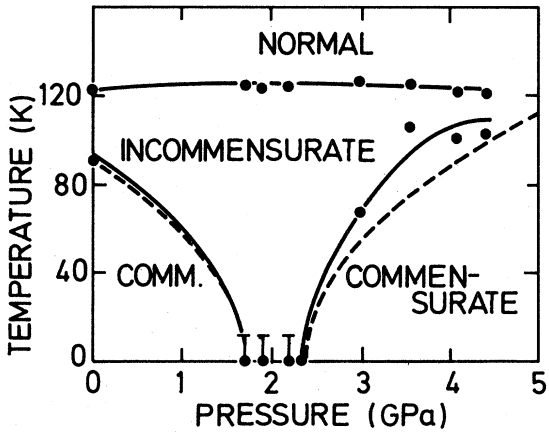

FIG. 1. The pressure-temperature phase diagram of the CDW phase in $2H$-$TaSe_2$. The points are the results of x-ray scattering experiments by McWhan and co-workers (Ref. 5) and the solid line is a guide to the eye. The dashed line in the empirical fit to the IC phase boundary described in Sec. IV A.

form was recently written down by Jacobs and Walker.[10] The detailed form of the I phase is also modified and as pointed out by Bak *et al.*,[11] this leads to either hexagonal or stripe configurations of DC in the I phase.

In this work we are interested primarily in the phase boundary and we shall take this to be determined by the energy to introduce a single DC and ignore the effects of interactions between the DC.

In Sec. II the general Landau expansion of the free energy in the C phase is the starting point. The discussion is limited to variations of the phases of the order parameters. The energies of small oscillations in the phases are evaluated and compared to the frequencies measured by Raman scattering.[12,13] There are several differences from the assignments and energies obtained by Holy *et al.*[12] Then the energy of a DC is calculated for the two principal directions under the assumption that only a single component of the phase varies in a DC. It is shown that the lines of DC are preferentially oriented parallel to the reciprocal-lattice vectors of the crystal, in agreement with experiment.

In Sec. IV A an empirical fit is made to the IC phase boundary and from this fit a minimum in the energy of a DC is obtained. A possible way to obtain such minimum by switching the intralayer phase variable from one minimum to another is presented in Sec. IV B. However the resultant minimum is too shallow when compared to that deduced from the phase boundary.

The conclusions are presented in Sec. V. It is suggested that the phase diagram at temperatures $T \lesssim 100$ K is influenced by impurities which pin the lines of DC and restrict their mobility.

II. LANDAU THEORY AT AMBIENT PRESSURE

The form of the Landau expansion of the free energy in $2H$-$TaSe_2$ has been discussed by several authors. The most complete discussion has been given in the recent paper by Jacobs and Walker.[10] Their form for the free energy density (a single layer) is

$$F[\Psi_i(\vec{x})] = A\sum_j |\Psi_j|^2 + G\sum_j |\Psi_j|^4 + \tfrac{1}{2}K\sum_{i\neq j} |\Psi_i\Psi_j|^2 + B\sum_j \left|\left(i\frac{\partial}{\partial x_{\parallel j}} + q\right)\Psi_j\right|^2$$
$$+ C\sum_j \left|\frac{\partial}{\partial x_{\perp j}}\Psi_j\right|^2 - \mathrm{Re}\left(\mathfrak{D}\Psi_1\Psi_2\Psi_3 + \mathcal{E}\sum_j \Psi_j^3 + \mathfrak{M}\sum_j \Psi_j^2\Psi_{j+1}^*\Psi_{j+2}^*\right) . \tag{2.1}$$

The three complex order parameters $\Psi_j (j = 1, 3)$ describe the three coexisting CDW in each layer. The charge modulation is given by

$$\delta\rho(\vec{x}) = 2\,\mathrm{Re}\left(\sum_j \Psi_j(\vec{x})\exp(i\tfrac{1}{3}\vec{G}_j\cdot\vec{x})\right) \tag{2.2}$$

and $\{\vec{G}_j\}$ are the three reciprocal short lattice vectors in the basal plane. The periodic lattice modulation is $\frac{1}{2}\pi$ out of phase with the charge modulation and is given by

$$\vec{\epsilon}(\vec{R}_i) = \mathrm{Im}\left(\sum_j \epsilon_0 \frac{\vec{G}_j}{|G_j|}\Psi_j(\vec{R}_i)\exp(i\tfrac{1}{3}\vec{G}_j\cdot\vec{R}_i)\right) \tag{2.3}$$

and ϵ_0 gives the amplitude of the lattice distortion.

The first three terms depend only on the moduli, $|\Psi_j|$. In order to simplify matters, we shall assume that the moduli are fixed and determined by minimizing these three terms. This leaves the phases of the individual CDW to be determined. The order-parameters can then be written as $\Psi_j(\vec{x}) = \exp[i\phi_j(\vec{x})]$ without loss of generality. The phases $\{\phi_j\}$ are determined by the last three terms in Eq. (2.1). The first of these is an intralayer phasing energy which depends only on the combination $\phi_1+\phi_2+\phi_3$. The other two terms are the commensurability terms which involve each individual phase. These latter terms describe the coupling of the position of each commensurate CDW to the position of the underlying lattice. Finally the fourth and fifth terms are the restoring forces when spatial variations of the phase are introduced. In the fourth term the occurrence of the wave vector q describes the possibility that the natural wave vector of the CDW may be slightly different to the commensurate value.

The parameters A, B, C, G, and K are real but $\mathfrak{D}$, $\mathcal{E}$, and $\mathfrak{M}$ are complex in general. A single layer of $2H$-TaSe does not have inversion symmetry. The $2H$ crystal structure has a center of inversion located halfway between the layers. Under inversion symmetry the charge $\delta\rho_\pm(\vec{x}) \rightarrow \delta\rho_\mp(-\vec{x})$ where the subscript $\{\pm\}$ denotes the layer, and the phases $\phi_{j\pm} \rightarrow -\phi_{j\mp}$ under inversion.[10] This leads to a form for the free energy of the second layer in which the replacement $\mathfrak{D}_+ \rightarrow \mathfrak{D}_-^*$, $\mathcal{E}_+ \rightarrow \mathcal{E}_-^*$, and $\mathfrak{M}_+ \rightarrow \mathfrak{M}_-^*$ is made in Eq. (2.1).

If we restrict ourselves to symmetries in which the CDW structure has the same periodicity along the c axis as the lattice, i.e., a double layer structure, then the phase parameters $\{\phi_{j\pm}\}$ associated with each of the three CDW ($j = 1, 3$) in each of the two layers ($\pm$) need to be determined. The part of the CDW free energy which depends on these phases can be written as

$$F\{\phi\}=B\int d^2x\sum_{j\pm}\left\{\left[\left(\frac{\partial}{\partial x_{\parallel j}}-q\right)\phi_{j\pm}\right]^2+\left(\frac{\partial}{\partial x_{\perp j}}\phi_{j\pm}\right)^2\right\}$$
$$+\int d^2x\Big[-D[\cos(\phi_{1+}+\phi_{2+}+\phi_{3+}+\gamma)+\cos(\phi_{1-}+\phi_{2-}+\phi_{3-}-\gamma)]$$
$$-E\sum_{j=1,3}[\cos(3\phi_{j+}+\chi)+\cos(3\phi_{j-}-\chi)]$$
$$-M\sum_{j=1,3}[\cos(2\phi_{j+}-\phi_{j+1,+}-\phi_{j+2,+}+\mu)+\cos(2\phi_{j-}-\phi_{j+1,-}-\phi_{j+2,-}-\mu)]$$
$$+2F\sum_{j=1,3}\cos(\phi_{j+}-\phi_{j-}-\alpha)\Big]\ , \tag{2.4}$$

where we have written $\mathfrak{D}\equiv D\exp(i\gamma)$; $\mathcal{E}=E\exp(i\chi)$, and $\mathfrak{M}=M\exp(i\mu)$. The last term is the interlayer coupling energy which arises from Coulomb coupling of the CDW and elastic coupling of the lattice distortions in two adjacent layers. In general a phase difference can arise from the elastic coupling and is allowed by symmetry.

It is convenient to replace the phase variables $\{\phi_{i\pm}\}$ of the individual CDW by a set of variables which describe the relative phasing of the CDW in each layer and the displacement of the CDW structure. These variables are

$$\phi_\pm=\tfrac{1}{3}(\phi_{1\pm}+\phi_{2\pm}+\phi_{3\pm})\ ,$$
$$\phi_{x\pm}=\tfrac{1}{3}(2\phi_{1\pm}-\phi_{2\pm}-\phi_{3\pm})\ , \tag{2.5}$$
$$\phi_{y\pm}=\frac{1}{\sqrt{3}}(\phi_{2\pm}-\phi_{3\pm})\ .$$

The $\phi_\pm$ variable describes the pattern formed by the intersection of the CDW, e.g., when $\phi_\pm=0$ the charge maxima of all three CDW coincide at a set of points. The other two variables describe displacements of the CDW structure, either parallel (ϕ_x) to a reciprocal-lattice direction $\{\vec{G}\}$ or perpendicular (ϕ_y). The inverse relations are

$$\phi_{1\pm}=\phi_\pm+\phi_{x\pm}\ ,$$
$$\phi_{2\pm}=\phi_\pm+\frac{\sqrt{3}}{2}\phi_{y\pm}-\tfrac{1}{2}\phi_{x\pm}\ , \tag{2.6}$$
$$\phi_{3\pm}=\phi_\pm-\frac{\sqrt{3}}{2}\phi_{y\pm}-\tfrac{1}{2}\phi_{x\pm}\ .$$

When substituted in Eq. (2.4) this leads to the following form for the phase dependent terms in the free energy of the commensurate phase.

$$F_c(\phi_\pm,\phi_{x\pm},\phi_{y\pm})=\sum_\pm\int d^2x\Big\{-D\cos(3\phi_\pm\pm\gamma)-E\Big[\cos(3\phi_\pm+3\phi_{x\pm}\pm\chi)+\cos\Big(3\phi_\pm+\frac{3\sqrt{3}}{2}\phi_{y\pm}-\tfrac{3}{2}\phi_{x\pm}\pm\chi\Big)$$
$$+\cos\Big(3\phi_\pm-\frac{3\sqrt{3}}{2}\phi_{y\pm}-\tfrac{3}{2}\phi_{x\pm}\pm\chi\Big)\Big]$$
$$-M\Big[\cos(3\phi_{x\pm}\pm\mu)+\cos\Big(\frac{3\sqrt{3}}{2}\phi_{y\pm}-\tfrac{3}{2}\phi_{x\pm}\pm\mu\Big)+\cos\Big(-\frac{3\sqrt{3}}{2}\phi_{y\pm}-\tfrac{3}{2}\phi_{x\pm}\pm\mu\Big)\Big]\Big\}$$
$$+\int d^2x\Big\{2F\Big[\cos(\phi_+-\phi_-+\phi_{x+}-\phi_{x-}-\alpha)+\cos\Big(\phi_+-\phi_-+\frac{\sqrt{3}}{2}(\phi_{y+}-\phi_{y-})-\tfrac{1}{2}(\phi_{x+}-\phi_{x-})-\alpha\Big)$$
$$+\cos\Big(\phi_+-\phi_--\frac{\sqrt{3}}{2}(\phi_{y+}-\phi_{y-})-\tfrac{1}{2}(\phi_{x+}-\phi_{x-})-\alpha\Big)\Big]\Big\}\ . \tag{2.7}$$

The total free energy is divided into the elastic energy F_{el} and F_c.

The lowest energy state is determined by minimizing the energy with respect to the variables $\{\phi_\pm,\phi_{x\pm},\phi_{y\pm}\}$. This leads to many possible stationary points. At atmospheric pressure it has been determined experimentally[3,12] that $\phi_{x\pm}\equiv\phi_{y\pm}\equiv 0$ and $\phi_\pm=\pm\phi_0$. The Raman scattering experiments of Holy *et al.*[12] show a pattern of selection rules consistent with a CDW state with inversion symmetry confirming this choice of variables. Therefore, the discussion will be limited to this class of CDW states.

With this restriction the form of F_c simplifies considerably to

$$F_c(\phi_0)=\int d^2x\,[-2D\cos(3\phi_0+\gamma)-6E\cos(3\phi_0+\chi) - 6M\cos\mu+6F\cos(2\phi_0-\alpha)]\ . \tag{2.8}$$

This can be further simplified to give the form

$$F_c(\phi_0)=\int d^2x\,[-2S\cos(3\phi_0+\beta)-6M\cos\mu +6F\cos(2\phi_0-\alpha)]\ , \tag{2.9}$$

where

$$\tan\beta=(D\sin\gamma+3E\sin\chi)/(D\cos\gamma+3E\cos\chi)$$

and

$$S=[D^2+9E^2+6DE\cos(\chi-\gamma)]^{1/2}\ .$$

The equilibrium value ϕ_0 is determined by minimizing Eq. (2.9)

$$\frac{\partial F_c}{\partial\phi_0}=0\ . \tag{2.10}$$

III. EXCITATIONS IN THE CDW STATE

A. Small oscillations: phasons

The discussion of excitations naturally splits into small oscillations, or phasons, and large amplitude excitations, or discommensurations. The small oscillations around the CDW state discussed above can easily be evaluated. They consist of two types: (a) oscillations of the ϕ variable about its equilibrium value ϕ_0; and (b) vibrations of the CDW around its location.

The restoring force for the former oscillation at the zone center is determined by substituting $\phi_+=\phi_0+\sigma_+$, $\phi_-=-\phi_0+\sigma_-$ in Eq. (2.7) and expanding the free energy per unit area in powers of σ_+, σ_-:

$$F_c=F_c(\phi_0)-(\sigma_++\sigma_-)^2 3F\cos(2\phi_0-\alpha) +\tfrac{1}{2}(\sigma_+^2+\sigma_-^2)9S\cos(3\phi_0+\beta)\ . \tag{3.1}$$

The two modes with eigenvalues $(\sigma_+\pm\sigma_-)$ have different forces and different symmetries. The mode in which the two layers vibrate out of phase ($\sigma_+ +_,\sigma_-$ mode) has A_{1u} symmetry and a frequency given by

$$M^*\omega_+^2=3S\cos(3\phi_0+\beta)-4F\cos(2\phi_0-\alpha)\ , \tag{3.2}$$

while the in-phase mode with A_{1g} symmetry is given by

$$M^*\omega_-^2=3S\cos(3\phi_0+\beta)\ . \tag{3.3}$$

The mass M^* is determined by the lattice kinetic energy of Ta and Se atoms and has been estimated by Holy *et al.*[12] as 206 amu. These results are similar to those obtained by Holy *et al.*[12] They used a less general Landau expansion in which the angles γ and χ were taken as 0 and π, respectively. The vibrational modes at the zone center in which the CDW structures oscillate around their equilibrium positions are obtained by expanding Eq. (2.7) for small ϕ_x or ϕ_y. The result for the free energy per unit area, is

$$F_0=F_c(\phi_0)-\tfrac{3}{2}F[(\phi_{x+}-\phi_{x-})^2+(\phi_{y+}-\phi_{y-})^2] \times\cos(2\phi_0-\alpha)+\tfrac{27}{4}(\phi_{x+}^2+\phi_{x-}^2+\phi_{y+}^2+\phi_{y-}^2) \times[E\cos(3\phi_0+\chi)+M\cos\mu]\ . \tag{3.4}$$

The modes are isotropic and do not depend on direction.

However as before the interlayer coupling term splits the in- and out-of-phase oscillations between the layers. The in-phase motion has E_{2g} symmetry and a frequency given by

$$M^*\omega_+^2=9[E\cos(3\phi_0+\chi)+M\cos\mu] \tag{3.5}$$

and the out-of-phase mode (E_{1u} symmetry)

$$M^*\omega_-^2=9[E\cos(3\phi_0+\chi)+M\cos\mu] -4F\cos(2\phi_0-\alpha)\ . \tag{3.6}$$

These results are similar to those obtained by Holy *et al.*[12] In their calculations the $M\cos\mu$ term was omitted.

Holy *et al.*[12] have assigned the phase modes to the lowest modes of E_{2g} and A_{1g} observed by Raman scattering. Further with their restricted Landau expansion they could obtain the coefficients E and D from the frequencies. However if the more general Landau expansion is used it is clear from Eq. (2.1) that there are more unknown parameters and the two frequencies observed in Raman scattering are not sufficient to determine the parameters.

The validity of their assignments[12] of the lowest modes as phase modes is also open to question. Steigmeier *et al.*[13] observed that the Raman active mode with E_{2g} at 50 cm^{-1} persists to high temperatures ($T\approx 100$ K) through the commensurate-incommensurate transition. Therefore it appears doubtful that it is the E_{2g} phase mode. A better as-

TABLE I. Phason normal modes of the CDW in 2*H*-$TaSe_2$

Symmetry	ω_{obs} (cm^{-1})	$M^*\omega^2$
E_{2g}	65	$9[E\cos(3\phi_0+\chi)+M\cos\mu]$
A_{1g}	44	$3S[\cos(3\phi_0+\beta)]$

signment[13] is to take the 65-cm^{-1} E_{2g} mode as the phase mode and to assign the 50-cm^{-1} mode as the E_{2g} amplitude mode. The frequencies and assignments of the phase modes that result are listed in Table I.

B. Nonlinear excitations: discommensurations

The boundary between the commensurate and incommensurate phases is determined by the energy to introduce a nonlinear phase excitation or discommensuration (DC) into the commensurate phase. In the CDW state of $2H$-$TaSe_2$ there are three phase variables ϕ, ϕ_x, ϕ_y as we have seen and it is possible to have discommensurations in any of these three variables. However it is straightforward to show that the incommensurate driving term—the part of the fourth term in Eq. (2.1) which is linear in q—does not couple to a discommensuration in ϕ. This driving term in a single layer can be rewritten as

$$-2Bq\sum_j \frac{\delta}{\delta x_{\parallel j}}\phi_j(\vec{x}) = -3qB\left[\frac{\delta\phi_x}{\delta x}+\frac{\delta\phi_y}{\delta y}\right] . \quad (3.7)$$

The elastic energy density terms, quadratic in the derivatives, are given in a single layer by

$$F_{el}(\phi,\phi_x,\phi_y) = \tfrac{3}{2}(B+C)\left[\left[\frac{\delta\phi}{\delta x}\right]^2+\left[\frac{\delta\phi}{\delta y}\right]^2\right]+\frac{3B}{4}\left[\frac{\delta\phi_x}{\delta x}+\frac{\delta\phi_y}{\delta y}\right]^2+\frac{3C}{4}\left[\frac{\delta\phi_x}{\delta y}-\frac{\delta\phi_y}{\delta x}\right]^2$$
$$+\tfrac{3}{8}(B+C)\left[\left[\frac{\delta\phi_x}{\delta x}-\frac{\delta\phi_y}{\delta y}\right]^2+\left[\frac{\delta\phi_x}{\delta y}+\frac{\delta\phi_y}{\delta x}\right]^2\right]+\tfrac{3}{2}(B-C)\left[\frac{\delta\phi}{\delta x}\left[\frac{\delta\phi_x}{\delta x}-\frac{\delta\phi_y}{\delta y}\right]-\frac{\delta\phi}{\delta y}\left[\frac{\delta\phi_x}{\delta y}-\frac{\delta\phi_y}{\delta x}\right]\right] . \quad (3.8)$$

These terms separate into terms involving only the intralayer phase ϕ and the displacement (ϕ_x,ϕ_y) and cross terms. The elastic energy of the displacements, second through fourth terms has compressional, shear, and rotational energies. The latter arising from the orientation of the CDW structure relative to the host lattice.

The two principal directions for DC are with the line of DC oriented either parallel a reciprocal-lattice vector [i.e., $\phi_x=\text{const}$, $\phi_y(y)$] or perpendicular to a reciprocal-lattice vector [i.e., $\phi_y=\text{const}$, $\phi_x(x)$]. The nonlinear potentials differ in these two cases and we shall discuss them in turn.

i. Line of DC parallel to $\{\vec{G}\}$. Making the simplest assumption namely that only ϕ_y varies along y the energy density relative to C phase, obtained by substituting $\phi_{y\pm}=\phi_y$, $\phi_\pm=\pm\phi_0$ in Eq. (2.7) is,

$$F_{DC}(\phi_y) = \int\left\{\tfrac{3}{4}(3B+C)\left[\frac{\delta\phi_y}{\delta y}\right]^2+2E\left[2\cos(3\phi_0+\chi)-\cos\left[3\phi_0+\chi+\frac{3\sqrt{3}}{2}\phi_y\right]-\cos\left[3\phi_0+\chi-\frac{3\sqrt{3}}{2}\phi_y\right]\right]\right.$$
$$\left.+2M\left[2\cos\mu-\cos\left[\frac{3\sqrt{3}}{2}\phi_y-\mu\right]-\cos\left[\frac{3\sqrt{3}}{2}\phi_y+\mu\right]\right]\right\}dy . \quad (3.9)$$

This can be combined at once to give

$$F_{DC}(\phi_y) = \int\left[\tfrac{3}{4}(3B+C)\left[\frac{\delta\phi_y}{\delta y}\right]^2+4[E\cos(3\phi_0+\chi)+M\cos\mu]\left[1-\cos\frac{3\sqrt{3}}{2}\phi_y\right]\right]dy . \quad (3.10)$$

This is the standard form for a commensurable potential. In the DC ϕ_y varies from $\phi_y=0$ (at $y=-\infty$) to $\phi_y=4\pi/3\sqrt{3}$ (at $y=+\infty$). The energy of the DC[7,14] is

$$F_{DC,y} = \tfrac{16}{3}\{(3B+C)[2E\cos(3\phi_0+\chi)+2M\cos\mu]\}^{1/2} . \quad (3.11)$$

ii. Line of DC perpendicular to $\{\vec{G}\}$. In this case we take only an x variation in ϕ_x. Substituting $\phi_{x\pm}=\phi_x$ and $\phi_\pm=\pm\phi_0$ in Eq. (2.7) gives a free energy density, relative to the C phase

$$F_{\mathrm{DC}}(\phi_x)=\int\left[\tfrac{3}{4}(3B+C)\left(\frac{\delta\phi_x}{\delta x}\right)^2+2[E\cos(3\phi_0+\chi)+M\cos\mu][3-\cos(3\phi_x)-2\cos(\tfrac{3}{2}\phi_x)]\right]dx \ . \tag{3.12}$$

This free energy density is more complicated than the usual form and we have not solved it analytically for the detailed shape of the DC. However it is easier to obtain the energy of a DC since the elastic and commensurability energies contribute equally to the total energy. Therefore

$$F_{\mathrm{DC},x}=4[E\cos(3\phi_0+\chi)+M\cos\mu]\int_{-\infty}^{+\infty}dx\{[3-\cos(3\phi_x(x)]-2\cos[\tfrac{3}{2}\phi_x(x)]\} \ , \tag{3.13}$$

$$=6(3B+C)[E\cos(3\phi_0+\chi)+M\cos\mu]^{1/2}\int_0^{4\pi/3}(3-\cos3\phi_x-2\cos\tfrac{3}{2}\phi_x)^{1/2}d\phi_x \ , \tag{3.14}$$

$$=8(\tfrac{1}{3})^{1/2}[\sqrt{6}+\ln(\sqrt{2}+\sqrt{3})][(3B+C)[E\cos(3\phi_0+\chi)+M\cos\mu]\}^{1/2} \ . \tag{3.15}$$

Comparing this energy with Eq. (3.11) we see that it is larger by a factor of ≈ 2.2. However in deciding which orientation of DC is favored in the incommensurate phase we must also note, that the total phase change of DC_x is $4\pi/3$ while that of DC_y is only $4\pi/3\sqrt{3}$. Thus the incommensurate driving term Eq. (3.7) favors DC_x by a factor of $\sqrt{3}$. Combining these factors leads to the preferred orientation of the DC as DC_y or parallel to a reciprocal-lattice vector. This is the orientation observed experimentally.[4] However, we must qualify this comparison by the comment, that this calculation was performed with the intralayer phase variable ϕ and the amplitudes held constant. Relaxing these assumptions involves the solution of coupled nonlinear equations which is more difficult and we shall not pursue this subject further.

IV. PRESSURE-TEMPERATURE PHASE DIAGRAM

A. Phenomenological fit

The *IC* phase boundary is determined by the balance of the incommensurate driving term [Eq. (2.1)] and the energy to introduce a single DC in the *C* phase. A measure of the former is given by the degree of incommensurability at the onset temperature. This is shown in Fig. 2(a) and it is seen to increase monotonically with pressure. Clearly this cannot be the source of the reentrant behavior. The energy to introduce DC is a function of the Landau parameters [see Eq. (3.11)] and it is clear that we must look to the possibility of a minimum in this energy to explain a reentrant phase diagram.

This idea can be carried further by parametrizing the phase diagram. The value of q has been measured in the region where the *I* phase is stable down to the lowest temperature and its behavior can be fitted

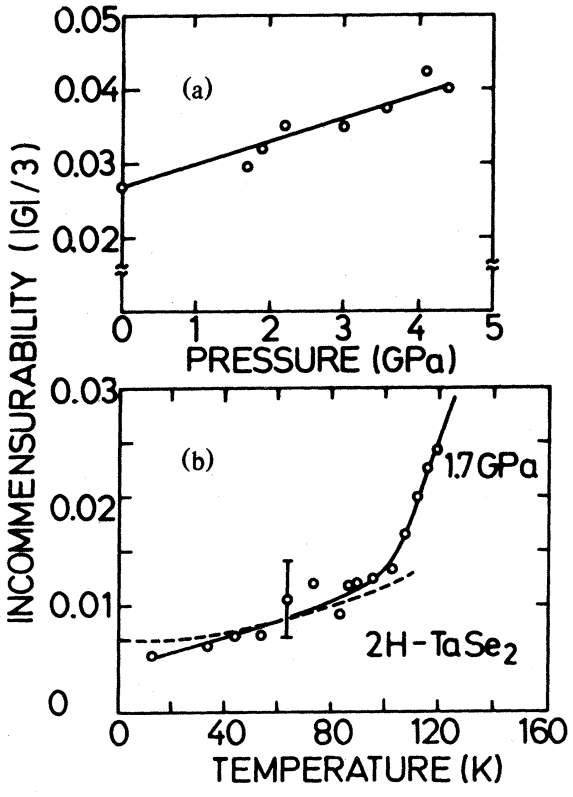

FIG. 2. The uppper part (a) shows the increase in the incommensurability at the onset temperature of the *I* phase with pressure. In the lower part (b), the temperature dependence of q is shown at a pressure of 1.7 GPa where the *I* phase is stable down to low temperatures. The points are the experimental results and the solid line is drawn through the points as a guide to the eye. The dashed line is the empirical fit described in Sec. IV A.

in the region of interest ($T \lesssim 100$ K) by a quadratic temperature dependence

$$q(T) = q_0(1 + aT^2) \tag{4.1}$$

with the values $q_0 = 7 \times 10^{-3}(G/3)$ and $a = 7 \times 10^{-5}$ K^{-2}. The fit is shown as the dashed line in Fig. 2(b). Since the pressure dependence of q is not essential we shall take this form as pressure independent.

The energy to introduce a DC as we shall see below may have a minimum at a cusp. This suggests that writing a form for the phase diagram

$$q_0(1 + aT_c^2) = y(P) \tag{4.2}$$

with $y(P)$ parametrized as

$$y(P) = y_0(1 + y_1|P/P_c - 1|) \tag{4.3}$$

with the choice of constants $y_0 = 6.3 \times 10^{-3}$ ($|G|/3$), $y_1 = 0.75$ and $P_c = 2$ GPa a reasonable fit to the phase diagram is obtained as shown in Fig. 1. This fit implies a fractional reduction of $\frac{4}{7}$ in the energy to introduce a DC between $P = 0$ and $P = P_c$.

B. Pressure dependence of the energy of a discommensuration

As discussed above, the key point is whether the energy to introduce a DC into the C phase can have a minimum. The parameter y in Eq. (4.3) is directly proportional to this energy for a DC_y

$$y = \frac{4}{\pi B}\{\tfrac{2}{3}(3B + C)[E\cos(3\phi_0 + \chi) + M\cos\mu]\}^{1/2} . \tag{4.4}$$

The main effect of pressure in $2H$-$TaSe_2$ is to reduce the interlayer separation and increase the interlayer coupling energy—the F term in Eq. (2.9). While this does not enter directly in Eq. (4.4) it enters indirectly through the value of ϕ_0 in Eq. (4.4). This value of ϕ_0 is determined by minimizing F [see Eq. (2.10)] leading to

$$S\sin(3\phi_0 + \beta) = 2F\sin(2\phi_0 - \alpha) . \tag{4.5}$$

The value of ϕ_0 has been discussed by several groups.[3,12,15,16] Brouwer and Jellinek[16] suggest that the neutron scattering experiments cannot easily distinguish between the values of $\phi_0 = 5\pi/4$ obtained originally by Moncton *et al.*[3,17] and the value $\phi_0 = \pi/4$ (which simply reverses all displacements) and argue for the latter choice. If we assume with Holy *et al.*,[12] that the interlayer couping is relatively small then we may take $4F \approx S$ in Eq. (4.5). This still leaves two phases α and β to be determined. A possible choice is illustrated in Fig. 3 which shows a graphical display of the two sides of Eq. (4.4). There are three solutions to Eq. (4.4) corresponding to

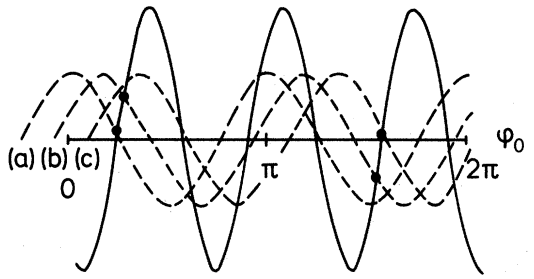

FIG. 3. The solid line and the dashed lines illustrate the left-hand side and the right-hand side of Eq. (4.5) for different values of the parameter α. The solid dots indicate the minimum energy solutions.

minima in F. Clearly to achieve the cusp minimum in $y(P)$ in Eq. (4.3), it is necessary that under pressure a switch is made from one minimum to another. A possible way to achieve this is illustrated in Fig. 3. If the phase α in the interlayer energy increases with pressure then the evolution shown in Fig. 3 takes us from a region ($P < P_c$) where ϕ_0 increases from $\pi/4$ to ≈ 1.0 radius and then switches abruptly (when $P > P_c$) to a value $\approx 3\pi/2$ radius and continues to increase. If we further assume a value of $\chi \approx \beta$ in Eq. (4.4), then in the first region ($P < P_c$) $\times\cos[3\phi_0(P) + \chi]$ will decrease from ≈ 1 [curve (a)] to a value ≈ 0.7 [curve (b)] while in the second region ($P > P_c$) $\cos[3\phi_0(P) + \chi]$ will now increase from ≈ 0.7 [curve (b)] again towards $+1$ [curve (c)]. The value of y will then decrease, pass through a cusp and then increase again as in Eq. (4.3). The only problem with this hypothesis is that the total change in $3\phi_0$ from $P = 0$ to $P = P_c$ is only ≈ 0.7 rad. This is not enough to make a large change in y, since we must assume, because of the high frequency of the E_{2g} mode discussed above, that the value of $M\cos\mu \approx E\cos(3\phi_0 + \beta)$ in Eq. (4.4). Making a crude estimate a drop of only $\approx 10\%$ is achieved in y between $P = 0$ and $P = P_c$ while the values obtained above from a fit to the phase diagram gave a value $\approx 40\%$. The conclusion is that the required qualitative behavior of $y(P)$ can be obtained but not quantitative agreement. Simply stated the problem is, that the commensurate phase has so many possible minima with different values of ϕ_0, and also possibly nonzero values of ϕ_x and ϕ_y, that it is hard to achieve a substantial reduction in the commensurability energy before another energy minimum becomes the absolute minimum.

V. CONCLUSIONS

The general form of the Landau expansion of the free energy of the CDW state has several terms with complex coefficients and the result is that there are

too many unknown constants to be determined by the observed Raman-active modes. As a result these constants cannot be determined from experiment.

In discussing the phase diagram under pressure, it is shown, that the reentrant behavior of the commensurate CDW can be explained if the energy to introduce a discommensuration goes through a minimum. Such a minimum can arise because of the several possible minima in the free energy with different values of the intralayer phase ϕ_0 and the possibility of switching the absolute minimum in energy from one of these minima to another. The result is a cusp in the energy of a DC versus pressure. This accounts qualitatively for the reentrant behavior of the commensurate phase. However, when quantitative estimates are made, it results in too shallow a minimum when compared with that deduced from the experimental phase diagram. One possibility for this discrepancy is that the observed phase diagram is strongly influenced by impurities. The *IC* transition at room pressure is found to have a large hysteresis[4] which implies restricted mobility of DC at temperatures $T \lesssim 100$ K. Therefore it may well be that the observed phase diagram is not in thermal equilibrium but instead the DC are pinned and the *I* phase persists down to low temperatures. McWhan and coworkers[5] have emphasized that a qualitative change occurs at temperatures ≈ 100 K. The model put forward here could be tested by making structural studies of commensurate phase under pressure to determine the variation of ϕ_0 with pressure. This proposed change in ϕ_0 with pressure would change the displacement pattern from that proposed in Ref. 16, in which there is a clustering of Ta atoms, to that proposed in Ref. 3, where the displacements are in opposite sense. Another test would be the observation of a reduced frequency of the Raman-active E_{2g} mode under pressure. This frequency however should remain finite at the *IC* boundary.

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